

SCIENCE FOR CERAMIC PRODUCTION

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USE OF DISTHENE-SILLIMANITE IN THE PRODUCTION OF POROUS PERMEABLE CERAMICS

S. A. Zhuravlev¹ and B. L. Krasnyi¹Translated from *Steklo i Keramika*, No. 5, pp. 17 – 19, May, 2004.

It is proposed to use porous ceramics made of a disthene-sillimanite concentrate as a filtering material in aggressive media; the effect of the plastic component (bentonite) on the properties of ceramics is analyzed; the results of studying the phase formation processes at 1250°C with different isothermal exposures are specified. It is established that disthene becomes mullitized at this temperature and the sillimanite structure becomes perfected.

The current production equipment of the chemical, mining, and other sectors of industry is operated in stringent conditions under the simultaneous impact of aggressive media, high temperature and pressure, and mechanical impacts. In such conditions ceramic products, primarily their surfaces, are destroyed as a consequence of two effects: corrosion fracture under the effect of an external environment and erosion fracture caused by mechanical impact [1].

Chemical equipment parts, including filtering porous ceramics operating in acid, alkali, and salt solutions, are subjected to the effect of the medium that dissolves ceramics. It is impossible to give a unique characteristic of the chemical resistance of a filtering material with respect to all possible reactants due to the diversity of the latter. A filtering material is usually assessed with respect to its resistance to aggressive media that it has to contact in service [2].

The majority of ceramics are more resistant to acid media (except for hydrofluoric and hot phosphoric acids) and less resistant to alkalis. The chemical resistance of various ceramic materials differs and depends on the chemical resistance of their components. There is a tendency to increase the content of mullite that has high acid resistance (99.4 – 99.8%) and alkali resistance (99.6%) to obtain a material with high chemical resistance.

Among inorganic acids, the most perceptible effect on ceramics, apart from hydrofluoric and phosphoric acids, is produced by hydrochloric acid. Sulfuric and nitric acids cause less corrosion. The most aggressive are medium- or high-concentration (50 – 80%) acids [3].

The chemical resistance of ceramics determined in accordance with GOST 473.1–81 and GOST 473.2–81 is shown in Table 1.

The most common filtering porous ceramics is chamotte-bentonite ceramics used for filtration and purification of gases, water, and various chemical reactants; its main properties are presented in Table 2 (TU U21-155–98).

The raw materials used for production of chamotte-bentonite ceramics are highly fired chamotte with water absorption not more than 1.0%, refractory clay, and bentonite clay. When a molded preform is fired, a mullite phase $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ is formed; at the same time a vitreous phase emerging along the grain boundaries binds the filler grains, but does not fill the pores and provides for open porosity in the material.

TABLE 1

Material	Acid resistance, %	Alkali resistance, %
Porcelain:		
hard	98.5 – 99.5	45 – 55
zircon	99.3 – 99.7	65 – 75
Ceramics:		
steatite	99.6 – 99.7	–
dunite	98.0 – 98.5	50 – 60
acid-resistant	95.0 – 98.0	–
porous (filtering)	95.0 – 98.0	90 – 92
chamotte-bentonite		
alumina (60 – 75% Al_2O_3)	99.3 – 99.5	86 – 95
oxide, highly alumina		
(over 90% Al_2O_3)	99.8 – 99.9	93 – 97

¹ Bacor Research Center Joint-Stock Company, Russia.

TABLE 2

Parameter*	Mass		
	21	32	43
Permeability coefficient, D	12 – 25	31 – 78	78 – 170
Apparent porosity, %	36	35	32
Prevailing pore diameter, μm	50 – 65	80 – 105	112 – 140
Compressive strength, MPa	27.5	21.0	21.0

* Acid resistance in all cases was 97%, alkali resistance was 90%.

TABLE 3

Porous ceramics with mass content of bentonite, %	Apparent density, g/cm^3	Open porosity, %	Compressive strength, MPa
<i>Exposure for 1 h*</i>			
10	1.95	38.5	42.1
15	2.00	36.1	77.6
20	2.04	34.0	59.8
<i>Exposure for 2 h*</i>			
10	1.94	40.1	40.5
15	1.96	36.5	88.9
20	1.99	34.8	76.8
<i>Exposure for 3 h*</i>			
10	1.83	41.5	44.1
15	1.86	39.6	63.2
20	1.91	36.5	64.8

* Isothermal exposure at 1250°C.

The high content of bentonite (25%, here and elsewhere mass content indicated) in chamotte-bentonite ceramics contributes to a substantial decrease in the effective pore radius of each monofraction and in the total porosity, which determines the permeability of filtering ceramics. A decrease in bentonite content lowers the strength of ceramics and leads to its untimely failure in service. An increased bentonite content causes a deformation of articles in firing. Furthermore, chamottizing of refractory clay and its subsequent crushing and screening by fractions for the purpose of obtaining monofractional powder involves additional power consumption. Therefore, it makes sense to use a natural material as a filler.

It can be seen from the data in Table 1 that alumina (60 – 75% Al_2O_3) ceramics containing minerals of the sillimanite group (disthene, sillimanite, and andalusite) is sufficiently resistant to the effect of aggressive media. The specified minerals, which have the common chemical formula $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (62.9% Al_2O_3 and 37.1% SiO_2), after firing at the respective temperatures transform into mullite. The theoretical yield of mullite is 86%, which is higher than in chamotte articles (approximately 50%); and the remaining 14% is silica, which under certain conditions may transform into silica glass or crystallize in the form of cristobalite.

All minerals of the sillimanite group differ in their physicochemical properties, including their crystallizing

structure and density. The mullite and the amorphous material formed after firing have a true density lower than that of the initial minerals, accordingly, they grow in volume after firing [4]. Moreover, the disthene-sillimanite concentrate DSK-3 has a virtually monofractional composition (about 93% fraction of 0.20 – 0.09 mm) [5], which makes it a suitable material for the production of filtering ceramics without additional treatment.

The use of disthene-sillimanite with naturally rounded particles whose roughness is minimum as a fractionated filler decreases the hydraulic resistance of the medium to be filtered and, consequently, increases the efficiency of the filtering equipment.

Thus, the properties of filtering ceramics can be improved using disthene-sillimanite concentrate.

Samples for analysis shaped as cylinders of diameter 36 and height 35 mm were produced by semidry molding on a hydraulic press at a pressure of 20 MPa. The firing was carried out in an electric furnace with silicon-carbide heaters in an oxidizing atmosphere. The petrographic studies were performed employing a POLAM R-211 polarization microscope in transmitted light with a total magnification of $\times 630$ using the immersion method to determine the distribution and composition of the phases.

The properties of disthene-sillimanite porous ceramics are listed in Table 3. It can be seen that with the quantity of bentonite increasing from 10 to 20% the open porosity decreases from 38.5 to 34.0, from 40.1 to 34.8, and from 41.5 to 36.5% for an exposure of 1, 2, and 3 h, respectively.

The filtering material after thermal treatment consists of disthene and sillimanite particles surrounded by the vitreous phase. The more glass in the material, the thicker is the film enveloping the grains. The vitreous phase in this case not only envelopes the particles, but fills the pores as well.

As the exposure duration at the maximum firing temperature of 1250°C increases, the porosity grows in all cases; however, its increase is not monotonic. With 10% bentonite the porosity grows nearly linearly, reaching 41.5% at an exposure of 3 h. For compositions with 15 and 20% bentonite with exposure extending from 1 to 2 h the porosity grows only by 0.4 – 0.8%, whereas under an exposure of 3 h it increases by 2 – 3% reaching 36.5 – 39.6%.

The changes in compressive strength are even more complex. This strength virtually does not change in the composition with 10% bentonite, whereas with 15 and 20% bentonite this strength reaches the maximum values under an exposure of 2 h. If the exposure is further extended to 3 h, the strength decreases.

Petrographic studies indicated that at 1250°C with an isothermal exposure for 1 h the surface of disthene becomes fully mullitized with the formation of thin needle-shaped mullite crystals up to 40 μm long and the vitreous material. The vitreous material formed from bentonite is located along the boundaries of disthene and sillimanite grains, abundantly wetting these grains and forming interlayers of thickness

4 – 12 μm . Within these interlayers one can see mullite with a chaotic crystallization and a needle size from 2 to 4 μm . The vitreous materials formed in mullitization of disthene and in vitrification of bentonite become intermixed and contact well with grains. However, with 10% bentonite occasional direct contact between disthene and sillimanite grains is registered. Increasing the quantity of bentonite to 20% leads to the formation of discontinuous interlayers from 1 to 30 μm thick, but without direct contacts between disthene and sillimanite. With an exposure for 3 h the phase composition does not change and the main structural modifications are related to the layout and thickness of the interlayers, which become uniformly distributed along the grain boundaries and have thickness of 10 – 20 μm . Furthermore, the sillimanite structure becomes perfected, which is manifested by a uniform value of birefringence from the periphery to the center of particles and its direct extinction.

The nature of the porosity variations indicate two simultaneous processes: transformation of disthene into mullite producing an increase in volume, and sintering, which decreases the porosity. A monotonic increase in porosity registered in samples with 10% bentonite agrees well with the literature data [6], according to which the linear sizes of disthene within the temperature interval of 1000 – 1450°C vary according to a near linear dependence and reach the maximum value of 12% at a temperature of 1450°C. In this case the vitreous phase formed in heat treatment does not fill the pores; however, the petrography analysis data show that

its quantity is insufficient to fix all contacts between the grains. An indirect proof of this is the decreased strength, which virtually does not vary with increasing isothermic exposure. For samples with 15 and 20% bentonite the increase in strength after 2-h exposure is related to the anticipated effect of the processes occurring in sintering. Under a 3-h exposure the growing porosity decreases the strength, which becomes virtually equal, indicating a perfected structure.

Thus, phase transformations occurring in the disthene-sillimanite concentrate in heating make it possible to produce filtering ceramics with predictable properties within sufficiency wide limits.

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